PHASE TRANSITIONS WITHOUT THERMODYNAMIC LIMIT

The Crucial Rôle of Possible and Impossible Fluctuations
The Treatment of Inhomogeneous Scenaria in the Microcanonical Ensemble

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1. Introduction

"In the thermodynamic limit the canonical and the microcanonical ensemble are equivalent in all details and generality." Statements like this are found in many textbooks of statistical thermodynamics. It is the purpose of this contribution to show that this is not so, and, more importantly, that the microcanonical ensemble allows for significant insight into the mechanism of first order phase-transitions which is hidden in the canonical ensemble. E.g.: at the liquid-gas transition under given pressure large and fluctuating spatial inhomogeneities are created. This surface entropy S_{surf} governs the surface tension. At the critical point $T_{cr}S_{surf}$ compensates even the surface energy of the ground state leading to the vanishing of the surface tension.

In the canonical ensemble at given pressure, however, inhomogeneities become suppressed by

$$\sim e^{-N^{2/3} f_{surf}/T_{boil}},\tag{1}$$

relative to the pure liquid or pure gas configurations, where N is the number of particles and f_{surf} the free energy of the interphase surface per surface atom. (In the following we use small letters for the energy or entropy per atom.) Consequently, macroscopic interfaces do not exist in the canonical ensemble.

This has a very practical consequence: "If phase transitions in the experimental world would be at constant temperature not under controlled supply of energy" i.e. energy constraints unimportant as is often claimed, we would not be able to see a pot with boiling water.

Other common wisdoms are: "Phase transitions exist only in the thermodynamic limit." This is certainly true within the canonical ensemble where phase transitions are indicated by a singularity point as functions of the temperature. For finite systems, however, the canonical partition sum

$$Z(T) = \sum_{i} e^{-Ne_i/T} \approx \int e^{N(s_N(e) - e/T)} N \ de.$$
 (2)

is analytic in $\beta = 1/T$. In the micro ensemble the transition occurs over a whole region in energy, relatively independent of the system size N.

"S must be additive (extensive). For microscopic objects like atoms and cosmic like stars thermodynamics is inappropriate !"/1| In contrast, I will show in the following that phase transitions are well defined and can be well classified into first order or continuous transitions for pretty small systems like nuclei or some 100-1000 atoms in the *microcanonical* ensemble. Moreover, for the liquid–gas transition in sodium, potassium, and iron the microcanonical transition temperature T_{tr} , the specific latent heat q_{lat} , and the specific interphase surface tension σ_{surf} are for ca. 1000 atoms close to their bulk values [2]. Nothing special qualifies the liquid–gas transition in infinite systems (at least for the above three realistic systems). This is also so in several toy-models of statistical mechanics: In [3] we found that for a microcanonical 2-dim Potts model with q = 10 states/latticepoint $T_{tr}, q_{lat}, \sigma_{surf}$ are within a few percent close to their bulk values for some hundred spins. This astonishing fast scaling of the microcanonical transition parameters with the particle number towards their bulk values was explained by Hüller and Promberger in a recent paper [4] by the fact that the trivial factor N in the exponent of the Laplace transform (2) is the main origin of canonical finite size scaling, which has nothing to do with the physics of the phase transition: Even if one replaces $s_N(e)$ in (2) by $s_{\infty}(e)$ of the infinite system one gets practically the same scaling of the specific heat with N.

In macroscopic thermodynamics extensive variables like total energy, mass, and charge are fixed only in the mean by the intensive T, μ_N , μ_Z [5]. In nuclear physics they are, however, strictly conserved. Nuclear systems are too small to ignore the fluctuations of conserved quantities when using the usual macroscopic thermodynamic relations as Hill suggests even if the fluctuations are somehow $\sim 1/\sqrt{N}$. Especially, if we are interested in phase transitions, we must be more careful: At phase transitions the effect of the fluctuations is usually even much larger, see below. Therefore, we test here statistical mechanics under extremely different conditions than we are used to. The foundations of thermodynamics must be revisited, extended and deepened. The constraints due to global conservation laws must carefully be respected and separated from the still persistent statistical fluctuations.

What is more remarkable and often overseen: Even in macroscopic systems statistical fluctuations/particle do not vanish and are usually large at phase-transitions of first order. I.e. even for phase transitions in the bulk (the standard field of thermodynamics) fluctuations and their constraints are important. Because it takes fluctuations serious our extended statistical thermodynamics can be applied to phase transitions in small as well in large systems. Especially the development of phase transitions with the size can then be followed from small to the bulk. Microcanonical thermodynamics even sheds new light on details of the mechanism leading to phase transitions in the bulk (sect.3). Moreover, in contrast to [1] it allows to address thermodynamically unstable like gravitating systems. There is some chance, this is possible even without invoking an artificial container.

Another example illuminates what I want to emphasize: Angular momentum is certainly one of the more exotic conservation laws in thermodynamics. In reality, however, it is much more important than one might think: In astrophysical systems like e.g. collapsing cosmic hydrogen clouds it may decide if a single star or a rotating multiple star system is born.

2. Microcanonical thermodynamics

Microcanonical thermodynamics explores the topology of the N-body phase space and determines how its volume $W(E, N) = e^{S}$ depends on the fundamental globally conserved quantities namely total energy E = N * e, angular momentum L, mass (number of atoms N), charge Z, linear momentum \mathbf{p} , and last not least, if necessary, the available spatial volume Vof the system. This definition is the basic starting point of any statistical thermodynamics since Boltzmann[6]. If we do not know more about a complicated interacting N-body system but the values of its globally conserved macroscopic parameters, the probability to find it in a special phase space point (N-body quantum state) is uniform over the accessible phase space. This is an *entirely mechanistic* definition. It is of course a completely separated and difficult question, outside of thermodynamics, if and how a complicated interacting many-body system may explore its entire allowed phase space. In a nuclear or cluster collisions it is not really necessary that every dynamical path visits the entire possible phase space. It is sufficient that the evolution of an ensemble of many replica, one after the other, of the same system under identical macroscopic initial conditions follows the structure of the underlying N-body phase space. It is ergodic in the same sense as the dynamics of a falling ball is ergodic on Galton's nailboard. In nuclear fragmentation the ergodicity is presumably due to the strong and short ranged friction between moving nuclei in close proximity. Friction between atomic clusters is yet unknown but probably it exists there also.

2.1) Statistical ensemble

Before we proceed, we have to emphasize the concept of the statistical ensemble under strictly conserved energy, angular momentum, mass, and charge. As we explained above, microcanonical thermodynamics describes the dependence of the volume e^S of the – at the given energy E, small interval δE , – accessible phase space on the globally conserved energy, mass, and charge. Each phase space cell of size $(2\pi\hbar)^{3N-6}$ corresponds to an individual configuration (event) of our system. We realize the ensemble by replica in time under identical macroscopic conditions (events). This is different from Hill [5] who assumes a macroscopic noninteracting supersystem of many identical copies of the system under consideration. This would be impossible e.g. for rotating or gravitating systems. Clearly, the volume e^S of the phase space is the sum (ensemble) of all possible phase space cells compatible with the values of energy etc..

While the conserved, extensive quantities, energy, momentum, number of particles, and charge can be determined for each individual configuration of the system, i.e. at each phase-space point or each event, this is not possible for the phase space volume e^S , i.e. the entropy S(E, V, N)and all its increments like the temperature $T = (\partial S(E, V, N)/\partial E)^{-1}$ the pressure $P(E, V, N) = T\partial S(E, V, N)/\partial V$, and the chemical potential $\mu = -T\partial S(E, V, N)/\partial N$. They are ensemble averages. Only in the thermodynamic limit $N \to \infty$ may e.g. the temperature be determined in a single configuration by letting the energy flow into a small thermometer. For a finite system, e.g. a finite atomic cluster, the temperature, its entropy, its pressure can only be determined as ensemble averages over a large number of individual events. E.g. in a fusion of two nuclei the excitation energy in each event is given by the ground-state Q-values plus the incoming kinetic energy whereas the temperature of the fused compound nucleus is determined by measuring the kinetic energy spectrum of decay products which is an average over many decays. It is immediately clear that the size of S is a measure of the *fluctuations* of the system.

2.2) Microcanonical signal for a phase transition: The caloric curve. The most dramatic phenomena in thermodynamics are phase transitions. I will try to interpret them microcanonically as peculiarities of the topology of the N-body phase space. I will avoid the concept of the thermodynamic limit as I believe that this is not really essential to understand phase transitions. We will see that details about the transitions become more transparent in finite systems. Then however, one needs a modified definition of phase transitions.

In [7, 8] we introduced a new criterion of phase transitions, which avoids any reference to the thermodynamic limit and can also be used

for finite systems: The anomaly of the microcanonical caloric equation of state T(E/N) where $\partial T/\partial E \leq 0$ i.e. where the familiar monotone rise of the temperature with energy is interrupted. Rising the energy leads here to a cooling of the system. This anomaly corresponds to a convex intruder in $S(E) = \int 1/T(E)dE$. At energies where S(E) is convex the system would spontaneously divide into two parts and gain entropy eg.: $(S(E_1) + S(E_2))/2 > S((E_1 + E_2)/2)$, iff the creation of the interface would not cost an extra entropy ΔS_{surf} . Because Δs_{surf} per atom vanishes $\propto N^{-1/3}$ in the thermodynamic limit $s_{\infty}(e)$ is concave as demanded by van Hove's theorem [9] and by the second law of thermodynamics.

Very early the anomaly of the caloric curve T(E/N) was taken as signal for a phase transition in small systems in the statistical theory of multi-fragmentation of hot nuclei by Gross and collaborators [7, 10] and the review article [11]. Bixton and Jortner [12] linked the back-bending of the microcanonical caloric curve to strong bunching in the quantum level structure of the many-body system i.e. a rapid and sudden opening of new phase space when the energy rises. Their paper offers an interesting analytical investigation of this connection.

A phase transition of first order is characterized by a sine-like oscillation, a "back-bending" of T(e = E/N) c.f. fig.1. As shown below, the Maxwell-line which divides the oscillation of $\partial S/\partial E = \beta(e) = 1/T$ into two opposite areas of equal size gives the inverse of the transition temperature T_{tr} , its length the specific latent heat q_{lat} , and the shaded area under each of the oscillations is the loss of specific entropy Δs_{surf} as mentioned above. The latter is connected to the creation of macroscopic interphase surfaces, which divide mixed configurations into separated pieces of different phases, e.g. liquid droplets in the gas or gas bubbles in the liquid. Even nested situations are found like liquid droplets inside of crystallized pieces which themselves are swimming in the liquid in the case of the solid - liquid transition, see e.g. the experiments reported in [13]. I.e. at phase transitions of first order inhomogeneous "macroscopic or collective" density fluctuations are common, boiling water is certainly the best known example. Phase-dividing surfaces of macroscopic size exist where many atoms collectively constitute a boundary between two phases which cause the reduction of entropy by Δs_{surf} .

2.3) "Maxwell" construction of T_{tr} , q_{lat} , σ_{surf} As the entropy is the integral of $\beta(e)$: $s(e) = \int_0^e \beta(e')de'$ it is a concave function of e ($\partial^2 s/\partial e^2 = \partial \beta/\partial e < 0$) as long as $T(e) = \beta^{-1}$ shows the usual monotonic rise with energy. In the pathological back-bending region of $\beta(e)$ the entropy s(e) has a convex intruder of depth Δs_{surf} [3]. At the beginning ($\geq e_1$) (c.f. fig.1c) of the intruder the specific entropy s(e) is reduced compared to its concave hull, which is the double tangent to s(e) in the points e_1 and e_3 . The derivative of the hull to s(e) follows the Maxwell-line in the interval $e_1 \leq e \leq e_3$. In the middle, (e_2) , when the separation of the phases is fully established this reduction is maximal $= \Delta s_{surf}$ and at the end of the transition (e_3) when the intra-phase surface(s) disappears Δs_{surf} is gained back. Consequently, the two equal areas in $\beta(e)$ are the initial loss of surface entropy Δs_{surf} and the later regain of it. Due to van Hove's theorem this convex intruder of s(e) must disappear in the thermodynamic limit which it will do if $\Delta s_{surf} \sim N^{-1/3}$. This is why a transition of first order may easier be identified in finite systems where the intruder can still be seen. The intra-phase surface tension is related to Δs_{surf} by $\gamma_{surf} = \Delta s_{surf} * N * T_{tr}/\text{surf}$ -area. [14]}.

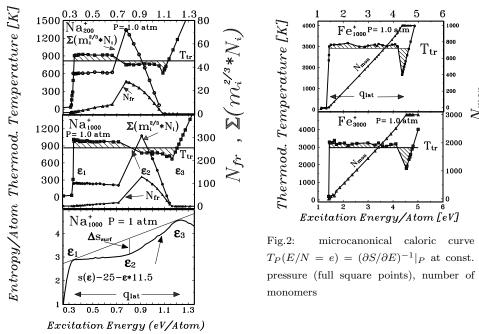


Fig.1: microcanonical caloric curve $T_P(E/N=e,V(E,P,N),N)=(\partial S/\partial E)^{-1}|_P$ at constant pressure (full square points), number of fragments N_{fr} with $m_i\geq 2$ atoms, and the effective number of surface atoms $N_{eff}^{2/3}=\sum m_i^{2/3}N_i=$ total surface area divided by $4\pi r_{ws}^2$. In the lower panel $s(e)=\int_0^e\beta(e')de'$ is shown. In order to make the intruder between e_1 and e_3 visible, we subtracted the linear function 25+11.5e.

2.4) Geometric vs. entropic classification phases and phase-boundaries Our approach to phase-transitions of first order is complementary to the conventional approach where the separation of the system into two homogeneous phases by a — in general — geometrical interface is investigated, e.g.[15]. The problems due to the large fluctuations of this interface are

numerous and severe, see e.g. the discussion on fluid interfaces by Evans [16]. These fluctuation are of course crucial for the interfacial entropy and consequently for the surface tension also.

The two main differences of our approach are that a) we do not start with the geometry (planar or spherical) of the interface, nor do we demand the interface to compact. We focus our attention to the entropy of the phase separation. This turns out to be much simpler than the geometric approach. b) The microcanonical ensemble allows for large scale spatial inhomogeneities, whereas the canonical ensemble suppresses spatial inhomogeneities like phase-separations exponentially. Any interface needs an additional free energy. {In the case of a phase transition of first order the suppression is $\propto exp(-\sigma N^{2/3}/T_{tr})$, where σ is the surface tension parameter $(\sigma = 4\pi r_{ws}^2 \gamma)$ and r_{ws} is the radius of the Wigner-Seitz cell.

Our characterization of phase transitions is purely thermodynamically. We have not yet defined what a phase is. Much effort is spent by Ruelle to define pure phases as those for which in the thermodynamic limit observables survive increasing coarse-graining, for which space-averaged quantities do not fluctuate, c.f. chapter 6.5 in Ruelle's book [17]. Of course, this definition works in the thermodynamic limit only. It does not address finite systems. For a finite system it is not possible to decide if a single configuration corresponds to a pure phase or not. The situation is analogous to the definition of the temperature, see above. Again to be a pure phase is a feature of the whole ensemble not of a single phase-space point (configuration). We offer a statistical definition of a pure phase: A configuration belongs to the ensemble of pure phases — including its fluctuations — at concave points of S(E) with $\partial^2 S/\partial E^2 < 0$.

2.5) The microcanonical constant pressure ensemble

The micro-canonical ensemble with given pressure {E,P,N} must be distinguished from the (in spirit) similar constant pressure ensemble {H,P,N} introduced by Andersen [18, 19, 20] where a molecular-dynamic calculation with the hypothetical Hamiltonian [19]

$$H(\lbrace r_i, p_i \rbrace, V, \dot{V}) = \frac{V^{2/3}}{2} \sum_{i=1}^{N} m \dot{r_i}^2 + \sum_{i=1}^{N} \sum_{i=1}^{N} \Phi(r_{ij} V^{1/3}) + \frac{M}{2} \dot{V}^2 + P_E V$$
 (3)

is suggested. Here V is the volume of the system, taken as an additional explicit degree of freedom, $\{r_i, p_i\}$ are the coordinates and momenta of the atoms scaled with the factor $V^{1/3}$, $\dot{r_i}$, \dot{V} the corresp. velocities, $\Phi(r_{ij})$ is the intra-atomic two-body potential, and M is a hypothetical mass for the volume degree of freedom. P_E is the given pressure. The total enthalpy H, atoms plus V-degree of freedom, is conserved, not the total energy E of the atoms alone.

This is very different to our micro-canonical approach with given E, V(E,P), N where the energy E of the atoms is conserved and the pressure is the correct thermodynamic pressure $(P(E,V)=T(E,V)\partial S/\partial V|_E)$. At each energy the volume V(E,P) is simultaneously chosen for all members of the ensemble by the condition that $T(E,V)\partial S(E,V)/\partial V|_E$ of the whole ensemble is the correct pressure. In this case there is a unique correlation between the energy E and the volume V which does not fluctuate within the ensemble even though the pressure is specified. At the given energy this is still the $\{E,V(E,P,N),N\}$ ensemble.

3. The liquid-gas transition of sodium, potassium, and iron

The microscopic simulation of the liquid—gas transition in metals is especially difficult. Due to the delocalisation of the conductance electrons metals are not bound by two-body forces but experience long-range many-body interactions. Moreover, at the liquid—gas transition the binding changes from metallic to covalent binding. This fact is a main obstacle for the conventional treatment by molecular dynamics [21].

In the macro-micro approach we do not follow each atom like in molecular dynamics, the basic particles are the fragments. Their ground-state binding energies are taken from experiments. The fragments are spherical and have translational, rotational, and intrinsic degrees of freedom. The internal degrees of freedom of the fragments are simulated as pieces of bulk matter. The internal density of states, resp. the internal entropy of the fragments is taken as the specific bulk entropy s(e) at excitation energies $e \leq e_{max} = e_{boil}$, which can be determined from the experimentally known specific heat of the solid/liquid bulk matter [22]. e_{boil} is the specific energy where the boiling of bulk matter starts. Details are discussed in [2, 14]. Then the metallic binding poses no difficulty for us and the metal — nonmetal transitions is in our approach controlled by the increasing fragmentation of the system. This leads to a decreasing mean coordination number when the transition is approached from the liquid side while the distance to the nearest neighbor keeps about the same. Exactly this behavior was recently experimentally observed [23, 24]. By using the microcanonical ensemble we do not prespecify the intra-phase surface and allow it to take any form. Also any fragmentation of the interface is allowed. It is the entropy alone which determines the fluctuations of the interface. Here we present the first microscopic calculation of the surface tension in liquid sodium, potassium, and iron.

The decay of potassium is in all details similar to that of sodium, fig. (1). Therefore we don't show here the corresponding figures. The liquid—gas

transition in iron is different from that of the alkali metals: Due to the considerably larger surface energy parameter a_s in the liquid drop formula of the ground-state binding energies of iron compared to alkali metals there is no multi-fragmentation of iron clusters at P=1 atm. Iron clusters of $N \leq 3000$ atoms decay by multiple monomer evaporation c.f. fig.2.

	N_0	200	1000	3000	bulk
	$T_{tr}[K]$	816	866	948	1156
	$q_{lat} [eV]$	0.791	0.871	0.91	0.923
Na	s_{boil}	11.25	11.67	11.2	9.267
	Δs_{surf}	0.55	0.56	0.45	
	$N_{eff}^{2/3}$	39.94	98.53	186.6	∞
	σ/T_{tr}	2.75	5.68	7.07	7.41
	$T_{tr} [K]$	697	767	832	1033
	$q_{lat} [eV]$	0.62	0.7	0.73	0.80
K	s_{boil}	10.35	10.59	10.15	8.99
	Δs_{surf}	0.65	0.65	0.38	
	$N_{eff}^{2/3}$	32.52	92.01	187	∞
	σ/T_{tr}	3.99	7.06	6.06	7.31
	$T_{tr} [K]$	2600	2910	2971	3158
	$q_{lat} [eV]$	2.77	3.18	3.34	3.55
\mathbf{Fe}	s_{boil}	12.38	12.68	13.1	13.04
	Δs_{surf}	0.75	0.58	0.77	
	$N_{eff}^{2/3}$	22.29	65.40	142.12	∞
	σ/T_{tr}	6.73	8.87	16.25	17.49

TABLE 1:Parameters of the liquid–gas transition at constant pressure of 1 atm. in a microcanonical system of N_0 interacting atoms and in the bulk. $s_{boil} = q_{lat}/T_{tr}$, it is interesting that the value of s_{boil} for all three systems and at all sizes is near to $s_{boil} = 10$ as proposed by the empirical Trouton's rule [25], $N_{eff}^{2/3} = \sum m_i^{2/3} N_i$, $N_i =$ multiplicity of fragments with m_i -atoms, and $\sigma/T_{tr} = N_0 \Delta s_{surf}/N_{eff}^{2/3}$. The bulk values σ/T_{tr} are adjusted to the input values of a_s taken for the T=0 surface tension from ref.[26] which we used in the present calculation for the ground-state binding energies of the fragments. T_{tr} is T_P not T_V . T_V comes even closer to the bulk value. Other inputs of the calculations are: gound state liquid drop parameters of all possible clusters and the bulk entropy/internal dof in the liquid phase at $e \leq \varepsilon_1$ (fig.1).

Table (1) gives a summary of all theoretical parameters for the liquidgas transition in clusters of $N_0 = 200 - 3000$ Na, K, and Fe atoms and compared with their experimental bulk values. The transition-temperature T_{tr} , the specific latent heat q_{lat} and the entropy gain of an evaporated atom s_{boil} are approaching the experimental bulk values. Δs_{surf} is the area under the back-bend of $\beta(e)$. $N_0 \Delta s_{surf}$ is the total entropy loss due to the interfaces equal to $\sum 4\pi r_{ws}^2 m_i^{2/3} N_i \gamma / T_{tr} = N_{eff}^{2/3} \sigma / T_{tr}$. Of course, the transition temperature T_{tr} and the latent heat q_{lat} of small clusters are smaller than the bulk values because the average coordination number of an atom at the surface of a small cluster is smaller than at a planar surface of the bulk.

4. Conclusion

We presented a formulation of statistical thermodynamics entirely from the principles of mechanics. By carefully distinguishing conserved quantities like the energy, or angular momentum from ensemble averaged quantities like entropy, temperature or pressure this formulation allows an application to small systems like nuclei or atomic clusters and to astrophysical systems.

The microcanonical statistics also gives a detailed insight into the nature of phase transitions. The liquid–gas transition in metals at normal pressure of 1 atm. is experimentally well explored. Therefore, it is a good test case for our ideas and computational methods of microcanonical thermodynamics. By allowing a system of N=200-3000 atoms to condense or fragment into an arbitrary number of spherical fragment clusters and into an arbitrary number of free atoms under a prescribed external pressure of 1 atm. we calculated by microcanonical Monte Carlo methods [14] the microcanonical caloric curve $\beta(e) = \partial s/\partial e = \langle \partial/\partial e \rangle$. The anomaly of T(e), where $\partial T/\partial e \leq 0$, signals the liquid–gas phase-transition in the finite system. The characteristic parameters T_{tr} , q_{lat} , and the surface tension σ_{surf} are for ~ 1000 atoms similar to the experimentally known values of the bulk liquid–gas transition.

This result is remarkable for several reasons:

- a) It proves that a phase transition of first order in a realistic continuous system can very well be classified in small mesoscopic clusters without invoking the thermodynamic limit. In fact, with the finite back-bending of T(E/N) the transition is easier recognizable than at $N \to \infty$.
- b) Consistent with similar results for statistical toy models [3] T_{tr} , q_{lat} , σ_{surf} are for astonishing small systems close to their bulk values. The mechanism leading to phase-transition has nothing to do with the thermodynamic limit.
- c) Even for a realistic metallic system with its long-range many-body interactions the Microcanoncal Metropolis Monte Carlo simulation method is

able to describe the liquid—gas phase transitions quite well. This is possible because we do not use molecular dynamics with a two-body Hamiltonian but use the experimental groundstate binding energies of the fragment clusters which of course take care of the metallic bonding of their constituents. d) The intra-phase surface entropy can be microscopically calculated. This was not possible up to now for metals. The surface tension per surface area can be determined if the intra-phase area is known. For the surface entropy the fluctuation and fragmentation of the surface are essential. At the liquid—gas transition of sodium and potassium clusters of sizes as considered here at normal pressure the intra-phase fluctuations are mainly due to strong inhomogeneities and clusterization. This is consistent with recent experimental evidence for the bulk [23, 24]. This result is encouraging to also compute the surface tension at higher pressure to see its vanishing towards the critical point.

- e) The success of the Microcanoncal Metropolis Monte Carlo sampling method to reproduce for small clusters (within $\leq 20\%$) the known infinite matter values of the liquid–gas transition is also a promising and necessary test of MMMC to describe nuclear fragmentation [11, 14] and to be able to get insight into the (critical) behavior of the nuclear matter liquid–gas transition. This is important as it is obviously not possible to compare the model with experimental data for nuclear matter.
- f) The division of the macroscopic observables of the N-body system into observables which can be determined at each phase-space point, in each individual realization of the microcanonical ensemble, i.e.: globally conserved quantities, energy, number of particles, charge, angular momentum, and into thermodynamic observables which refer to the size of the ensemble, the $volume\ e^S$ of the energy shell of the phase space, and which cannot be determined at a single phase-space point, in a single event, like entropy, temperature, pressure, chemical potential is very essential. The concept of a pure phase and of a phase-transition belongs to the second group.
- g) Last not least, there is a very fundamental difference in the microcanonical and the canonical ensembles. The energy is the crucial parameter that controls the fluctuations in their development from the liquid to the vapor and this is respected only in the micro-ensemble.

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References

- Elliott H. Lieb and J. Yngvason. A guide to entropy and the second law of thermodynamics. cond-mat/9805005, 1998.
- 2. D.H.E. Gross and M.E. Madjet. Fragmentation phase transition in atomic clusters IV the relation of the fragmentation phase transition to the bulk liquid-gas

- transition. Z.Physik B, 104:541-551 and http://xxx.lanl.gov/cond-mat/9707100, 1997.
- 3. D.H.E. Gross, A. Ecker, and X.Z. Zhang. Microcanonical thermodynamics of first order phase transitions studied in the potts model. *Ann. Physik*, 5:446–452, 1996.
- M. Promberger. On a trivial aspect of canonical specific heat scaling. preprint, Erlangen, 1996.
- T.L. Hill. Thermodynamics of Small Systems I+II. W.A.Benjamin Inc., New York, Amsterdam, 1964.
- Ludwig Boltzmann. Vorlesung über Gastheorie. Number 1. Akademische Druck-u. Verlagsanstalt, Graz, 1981.
- D.H.E. Gross, X.Z. Zhang, and S.Y. Xu. Decay of very hot nuclei. Phys. Rev. Lett, 56:1544, 1986.
- 8. D.H.E. Gross, M.E. Madjet, and O. Schapiro. Fragmentation phase transition in atomic clusters I microcanonical thermodynamics. *Z.Phys.D*, 39:75–83;http://xxx.lanl.gov/cond-mat/9608103, 1997.
- 9. L. van Hove. Quelques propriétés générales de l'intégrale de configuration d'un système de particules avec interaction. *Physica*, 15:951, 1949.
- X.Z. Zhang, D.H.E. Gross, S.Y. Xu, and Y.M. Zheng. Decay of very hot nuclei, II, microcanonical metropolis sampling of multifragmentation. *Nucl. Phys.*, A 461:668–690, 1987.
- D.H.E. Gross. Statistical decay of very hot nuclei, the production of large clusters. Rep. Progr. Phys., 53:605–658, 1990.
- M. Bixton and J. Jortner. Energetic and thermodynamic size effects in molecular clusters. J. Chem. Phys., 91:1631–1642, 1989.
- M. Grimsditch and V.G. Karpov. Fluctuations during melting. J. Phys.: Condens. Matter, 8:L439–L444, 1996.
- D.H.E. Gross. Microcanonical thermodynamics and statistical fragmentation of dissipative systems — the topological structure of the n-body phase space. *Physics Reports*, 279:119–202, 1997.
- 15. A. Z. Panagiotopoulos. Mol. Phys., 61:813, 1987.
- R. Evans. Density functionals in the theory of nonuniform fluids. In D. Henderson, editor, Fundamentals of Inhomogeneous Fluids, chapter 3, pages 85–200. M. Dekker, Inc. New York, 1992.
- D. Ruelle. Statistical Mechanics, Rigorous Results. W.A.Benjamin, New York, Amsterdam, 1969.
- 18. H.C. Andersen. J. Chem. Phys., 72:2284, 1980.
- D. Brown and J.H.R. Clarke. A comparison of constant energy, constant temperature and constant pressure ensembles in molecular dynamics simulations of atomic liquids. Mol. Phys., 51:1243–1252, 1984.
- P. Procacci and B.J. Berne. Multiple time scale methods for constant pressure molecular dynamics simulations of molecular systems. Mol. Phys., 83:255-272, 1994.
- B.C. Allen. Surface tension. In R.W. Ohse, editor, Handbook of Thermodynamic and Transport Properties of Alkali Metals, chapter 6.8, pages 691–700. Blackwell Scientific, Oxford, 1985.
- D.H.E. Gross and P.A. Hervieux. Statistical fragmentation of hot atomic metal clusters. Z. Phys. D, 35:27–42, 1995.
- F. Hensel. The liquid..vapour phase transition in fluid mercury. Advances in Physics, 44:3–19, 1995.
- M. Ross and F. Hensel. A modified van der waals model for the coexistence of expanded metals. J. Phys.: Condens. Matter, 8:1909-1919, 1996.
- F. Reif. Fundamentals of statistical and thermal physics. McGraw-Hill, New York, 1965.
- C. Bréchignac, Ph. Cahuzac, F. Carlier, M. de Frutos, J. Leygnier, J.Ph Roux, and A. Sarfati. Dissosiation and binding energies of metal clusters. *Comments At. Mol. Phys.*, 31:361–393, 1995.